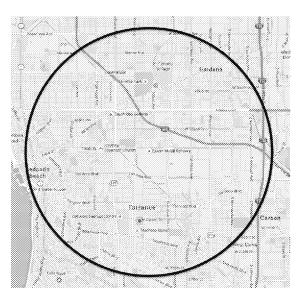


#### **EPA RMP Reports Understate MHF's Risk**

- 1. It's impossible that both the Valero Wilmington & Torrance RMP MHF reports could be correct
- Valero's release is 10.6 X greater than XOM's, yet the endpoint distance is only 1.3 X longer.
- 2. Valero's & ExxonMobil's toxic endpoint distances are far too short for MHF, which is 90% HF
- Among HF-using refineries in the US, the median endpoint toxic distance is 15 miles. Nearly half are over 20 miles.
- Valero, Wilmington & Quest Consultants state that MHF reduces toxic distances by just 7.9% compared to HF.



#### MHF: 90% HF 10% sulfolane

ExxonMobil: Current RMP Report 5,200 lb. release 3.2 mile toxic distance

Mobil's 1999 RMP Report 50,000 lb. (9.6 X more) 3.2 mile toxic distance (same)

Valero, Wilmington 55,000 lb. release 4.3 mile toxic distance (10.6 X Release Amount, 1.3 X Distance) Constant Con

Sally Hayati, TRAA

.



# Torrance Release Amount is Too Low by Nearly an Order of Magnitude

#### EPA Risk Management Program (RMP) offsite consequence analysis (OCA) worst case scenario (WCS)

- Facilities using a federally regulated substance over a threshold amount must submit a report
- MHF is a federally regulated substance in amounts exceeding 1,000 lb. EM has 250,000 lb.
- Worst-case scenario: calm atmospheric conditions, failure of *active* mitigation measures like water suppression systems, the release, over 10 minutes, of *the largest quantity of MHF* contained in a single vessel or interconnected process lines.

The largest amount MHF in a single vessel at Torrance is 50,000 lb., not 5,200 lb.

#### REFERENCES

- Living Safely With Chemicals, Understanding Chemical Risk Management, June, 1999, CAER leaflet, Mobil Oil Company, Modified Hydrogen Fluoride (MHF). From a participant in CAER in 1999. 50,000 lb. MHF in "reaction settler vessel." Page 3. <a href="http://bit.ly/1SV5vMs">http://bit.ly/1SV5vMs</a>.
- Workshop regarding ExxonMobil's use of MHF catalyst, City of Torrance Staff Report, October 13, 2015, Pg. 27, 1997 Briefing by TFD Chief R. Scott Adams: Acid Settlers contain largest amount MHF "in process:" 6,100 gallons x 8.3 lb./gallon =50,630 lb. <a href="http://torrance.granicus.com/MetaViewer.php?view">http://torrance.granicus.com/MetaViewer.php?view</a> id=8&event id=2620&meta id=236223>.

#### Both Toxic Endpoint Distances Are Too Short for 90% HF

EPA Risk Management Program Guidance for Offsite Consequence Analysis
Reference Table 7, Dense Gas Distances to Toxic Endpoint (a conservative but rational estimate)

- HF toxic endpoint given as 0.016 mg/L
- Release Amount (lb.) ÷ 10 (min) = HF release rate
- MHF distance (Col. 3) estimated as 7.9% less than HF distance (Col. 2) found using Table 7.

#### REFERENCES:

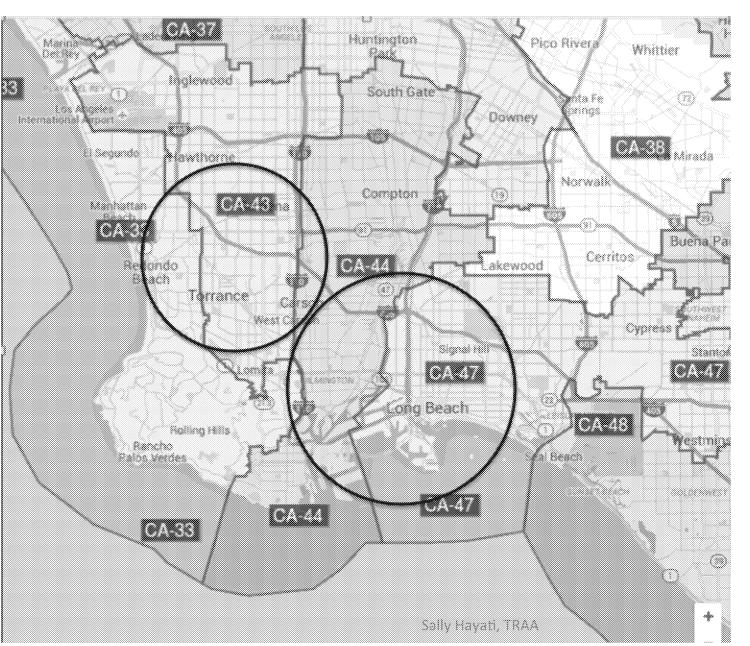
- 1. EPA, Risk Management Program Guidance for Offsite Consequence Analysis, 2009, <a href="http://www2.epa.gov/sites/production/files/2013-11/documents/oca-chps.pdf">http://www2.epa.gov/sites/production/files/2013-11/documents/oca-chps.pdf</a>.
- 2. "Quest, using ...an improved version of SLAB [dense gas modeling tool] and ... the proprietary physical properties of ReVAP (MHF)... determined that the maximum hazard distance for a worst case release of MHF is reduced by 7.9% over an equivalent HF release." Dr. Ron Koopman, HF expert, Goldfish Series Director.
- 3. "The implementation of the ReVAP process [MHF developed by Mobil] results in an 7.9% reduction in the maximum hazard distance."

Valero, Wilmington Final EIR for Alkylation Improvement Project, 2004, Appendix C, Hazard Analysis.

Refinery 1. R	elease Size (lb.) 2. HF	Distance (mi) 3. MH	F Distance (mi) 4	. Official RIVIP (mi)
ExxonMobil	5,200	5.3	4.9	<b>←</b> → 3.2
Mobil ('99)	50,000	16.4	15.1	<b>←</b> →→ 3.2
Valero	55,000	16.8	15.5	<b>←</b> 4.3

Why the huge discrepancy? Excess "passive mitigation credit" allowed for MHF + barriers, plus few constraints on the modeling method employed to estimate cloud travel distance.

#### Official Worst Case Scenario MHF Risk Zones in South Bay



#### **2 MHF RISK ZONES**

Valero, Wilmington TRC, Torrance Cover the South Bay

5,200 lb. Torrance release, calm day, no active mitigation, urban conditions

3.2 mi radius zone (black, L) of serious & irreversible health effects possible with short term exposure (> 20 ppm, ERPG-2)

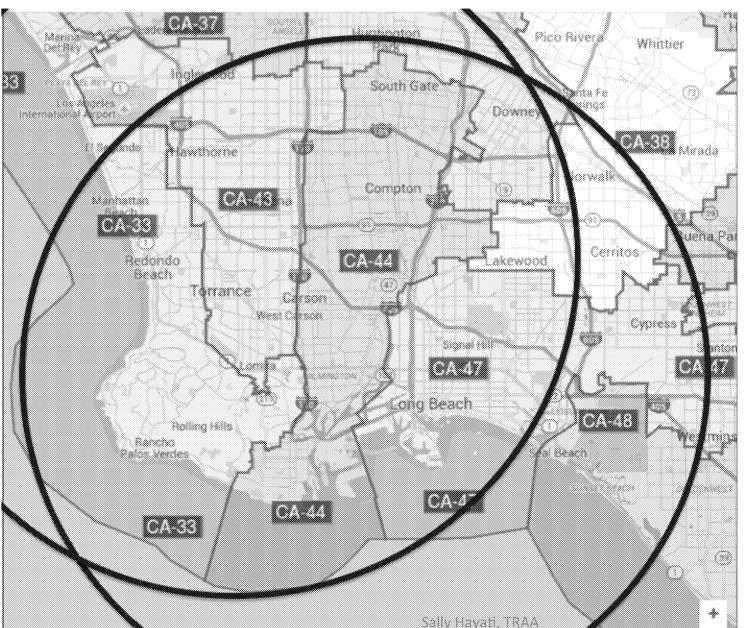
55,000 lb. MHF Valero. Same conditions

4.3 mi radius zone (black, R) of serious & irreversible health effects possible

Exposure to HF plume depends on wind direction.

(

#### Realistic Worst Case Scenario MHF Risk Zones in LA County



#### **2 MHF RISK ZONES**

Valero, Wilmington TRC, Torrance Touch nearly every LA County Congressional District

Each: ~50,000 lb. MHF released, calm day, no active mitigation, urban conditions.

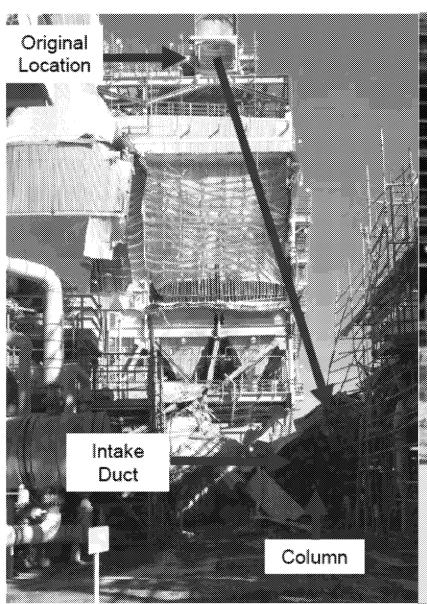
#### Exposure to HF plume depends on wind direction.

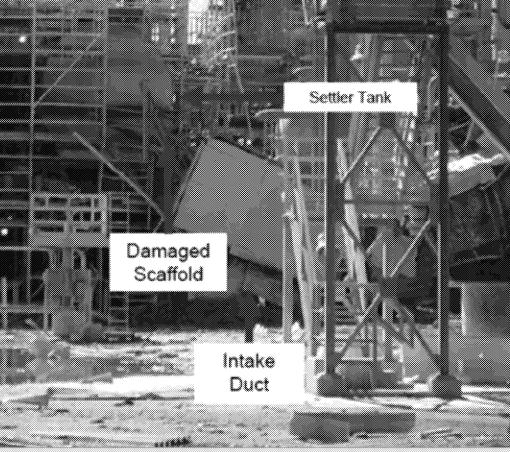
~15 mi radius zone (black) of serious & irreversible health effects possible with short term exposure (> 20 ppm, ERPG-2)

~7 mi. radius zone (inside each zone, not shown) lifethreatening health effects possible w/ short exposure (> 50 ppm, ERPG-3)

USW says nearly ½ of HF refineries in the US have > 20 mi radius risk zones.

#### Such an Accident Nearly Happened Feb. 18, 2015





Vanessa Sutherland, Chemical Safety Board (CSB) Chair: "We were really, really lucky... [This was] a near miss... It could have been much more catastrophic." An 80,000 lb. piece of equipment was sent flying during the explosion, landing 3 feet from 50,000 lb. of MHF in acid settler tank.

Saliy Hayati, TKAA

# Mitigation credit shouldn't be allowed for MHF *or* Mobil's Proprietary Barrier Technology

Passive mitigation measures function identically during transport, storage, use, regeneration, under all conditions with no human or mechanical energy input.

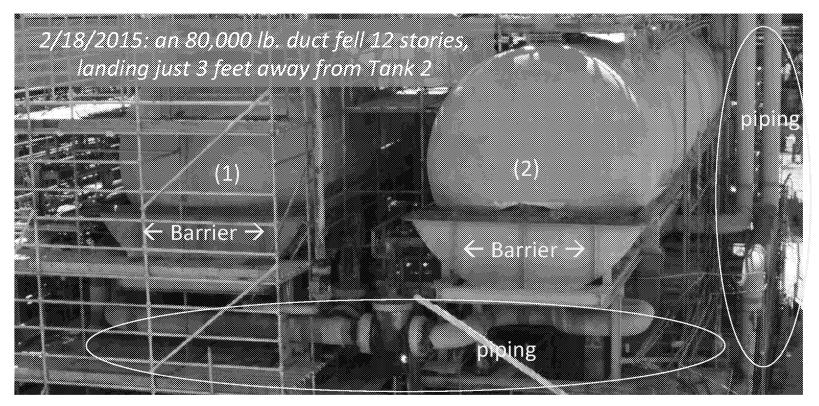
#### MHF requires routine human and mechanical energy input to maintain: it's not a "passive" measure

- MHF cannot be relied on to perform consistently through all phases regardless of management decisions, human error, or mechanical failure
- Additive consistently separates from HF during processing, during which time pure HF is present.
- Separated additive is "recovered" from the alkylate (the product) & the acid soluble oil (byproduct)
- Recovered additive must be recombined with HF in the proper ratio.
- Varying amounts of additive and HF are recovered. Unless care is taken, variation will occur in the ratio between recycled additive and HF, so "mitigation" value of MHF can easily vary cycle to cycle.
- MHF additive interferes w/ alkylation. Its only value is greater "safety."
- That's why the additive was slashed to a useless 10% after the MHF unit failed on startup in late 1997

#### Mobil proprietary barrier technology was hastily installed early 1998 to maintain a pretense of safety. Valero appears to make the same claim since MHF adoption in 2005 (passive mitigation MHF + barriers)

- Unverified safety claim: virtually all released HF will rain out upon striking barriers and stay down
  - But HF expert Dr. Koopman explains that any "rained out" acid would quickly vaporize.
- Furthermore, barriers were applied only to 2 areas on the Torrance alkylation unit
  - Seals of acid recirculation pumps
  - Bottom portion of the acid settler tanks
- No other alky unit components have barriers to "protect" against a MHF release there, including:
  - piping, top half of acid settler tanks, reactor, HF and additive recovery & regeneration elements.
  - The 2/18/2015 near miss on 50,000 lb. MHF was a location that had NO BARRIER.

#### Mobil's Proprietary Barrier Technology Shouldn't Receive Mitigation Credit



CSB's photo of alkylation unit Acid Settlers (1) and (2), each containing 50,000 lb. of MHF plus hydrocarbons. ExxonMobil claims the tanks are impervious. So... why put a barrier at the tank bottoms to control releases that can't happen?.... The piping (marked) certainly isn't impervious. At Marathon in 1987, 65K lb. HF was released after falling equipment broke a 2" pipeline... ExxonMobil claimed MHF wouldn't be released if a hole opened in the tank top, because HF settles to the tank bottom. But MHF/HF is "liquid under pressure" in the tank. Typical settler temperature is 105°F. MHF's boiling point is 73°F (10% additive). A tank breach would reduce the pressure; MHF would form a gas and flash out. Hydrocarbons have a lower boiling point, so would also flash and take HF with it.

#### Summary of Findings from TRAA's MHF Investigation

-See Appendix for Details and Supporting Evidence-

- MHF is 90% HF and 10% Sulfolane
  - The same MHF brand (originally ReVAP) is used by the Torrance & Valero Wilmington refineries
- ~90% of released MHF will form an HF cloud that is ~80% aerosol and 20% vapor
  - The HF cloud can remain dense and drift at ground level
  - "Mitigation" credit, if given (none is warranted), should be 10%, or no more than generous 15%
- Mobil's proprietary barrier technology, at best, reduces the rate at which MHF becomes airborne, and can only marginally reduce the HF cloud concentration
  - Virtually any "rained out" MHF will vaporize from the ground; it doesn't stay put. (Dr. Koopman)
  - Many/most releases will occur in areas of the alky unit not covered by a barrier
  - Mobil never tested the barrier configuration used at Torrance. The SW model Mobil used to estimate barrier performance wasn't accurate for very closely placed barriers or MHF w/ 10% additive, which forms an aerosol at temps only 6°F greater than pure HF itself. (Dr. Harpole)
  - No mitigation credit should be allowed for Mobil's proprietary barrier technology

Investigator: Sally Hayati, MS/PhD Electrical Engineering, USC, BS/MS biological sciences, Berkeley. Findings examined and corroborated by:

- Dr. Ronald Koopman, HF expert, Test Director for the 1986 Goldfish and 1988 Hawk HF Release Tests in NV desert, Former Liquid Gaseous Fuels Program Leader at Lawrence Livermore Lab
- Dr. Rafael Moure-Eraso, Chemical Engineer and former Chairman of the Chemical Safety Board
- Dr. George Harpole, Chief Engineer Northrop Grumman Aerospace Systems, Torrance resident
- Dr. Antonia Churg, retired Physical Chemist and Torrance resident

#### Don't Let This Happen in the South Bay!

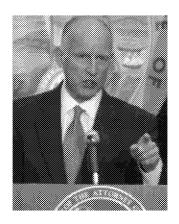


2012 HF Release S. Korean Chemical Plant

- Wind carried HF cloud *away from the city*. Our refinery's surrounded by city; it'd be worse here.
- 16,000 lb. released, 5 killed, 18 severely injured, 12,243 treated, thousands evacuated for weeks.
- Cattle and crops died. The area around the plant was declared a 'special disaster zone.'
- 80 other firms in the area were affected, with large business losses. Property values plunged.

Sally Hayati, TRAA

## Against MHF



MHF [is] an extremely toxic and volatile compound that can pose a risk to the public health ... [E]liminat[ing] the use of hydrofluoric acid in any form, [would be] a very substantial benefit....the use of MHF should be avoided when...there is a viable alternative.

Office of (then) CA Attorney General Jerry Brown, 2008

[The] use [of] "modified HF acid" for alkylation is a strategy that I oppose vigorously. This is an approach the majority of the refining industry does not use. There have been good options from the beginning [namely, sulfuric acid] ...There are those in the industry that cling to their belief in "modified HF acid" and the supporting technology. Most of those advocates either sell the design or license it. ...When all else fails, the advocates for such a strategy resort to the claim that...the two acids are equally safe."



Donald Hall, former refinery manager for the Big West in Bakersfield & Texaco's Los Angeles plant, 2008

[The February 18 explosion at the Torrance Refinery was a] "near miss" [on the MHF tank.] "It could have been much more catastrophic... If I were in the community I absolutely would be concerned."

Vanessa Sutherland, Chemical Safety Board Chair, 2015.

Details and supporting evidence

# THE TECHNICAL CASE AGAINST MHF AND MOBIL'S BARRIER TECHNOLOGY

## Torrance is Allowed Excess Credit for "Passive Mitigation"

-MHF + Release Barriers-

ExxonMobil takes roughly 71% mitigation credit MHF + barriers

Virtually none is warranted, and certainly no more than 10%-15%

How to roughly estimate the mitigation credit assumed by ExxonMobil:

EPA model RMP\*Comp: toxic endpoint distance Table 7, HF toxic endpoint 0.016 mg/L (ERPG-2)

- ExxonMobil's scenario: 5,200 lb. MHF w/in 10 minutes. 520 lb./min. MHF release rate
- Effective HF release rate = MHF release rate mitigation taken for (barriers + MHF)
- Given the ExxonMobil toxic distance of 3.2 miles & based on Table 7, the effective HF release rate EM used was ≈ 150 lb./min., 71% less than the MHF release rate.

Other than TRAA's, no independent investigation into MHF safety claims has been made since the operational failure of the first MHF unit w/ 30% additive, the secret slashing of additive to 10%, and the hasty addition of "innovative" proprietary barriers.

#### No Proprietary Justification for MHF Secrecy

-Trade Secrecy Claims Should Require Substantiation-

Emergency Planning and Community Right-to-Know Act (EPCRA), Substantiating claims of trade secrecy Code of Federal Regulations Title 40, Section 350.7 (40 CFR 350.7) Paragraph (a) substantiation questions:

- (4) The information should be a **secret of interest to competitors**There is no MHF competitor: Honeywell has a monopoly, and since any refinery may purchase it, the refinery itself has no claim to trade secrets for MHF.
- (4)(ii) Information claimed as trade secrets shouldn't be **publicly revealed.**The information is found in patents, material safety data sheets, risk management reports, and news articles on the Internet. (See following charts.)
- (4)(iv) The information should be **valuable information to competitors.**No MHF competitors exist. And if any arise, they'd find the information on-line.
- (5) Disclosure should cause **substantial harm to claimant's competitive position**.

  Not remotely true, for either Honeywell or ExxonMobil.

#### COMMUNITY RIGHT TO KNOW

-The Additive for the Mobil/Phillips MHF (ReVAP) is SULFOLANE-

Multiple patents reveal what the additive is. For example:

"In order to improve the safety factors of the HF alkylation process, one option is to operate with a vapor suppressant additive in the alkylation acid. ... A number of different sulfones have been proposed for this purpose but the one generally preferred is **sulfolane**"

HF alkylation process with acid regeneration, US Patent 7847142 B2, ExxonMobil Research and Engineering Company, 2007 (filing date), <a href="http://www.google.com/patents/US7847142">http://www.google.com/patents/US7847142</a>

Honeywell Material Safety Data Sheet for MHF reveals what the additive is. <a href="http://bit.ly/21T6yAt">http://bit.ly/21T6yAt</a>.

Component CAS-No. Weight percent

Hydrogen fluoride 7664-39-3 90.00%

Tetrahydrothiophene 1,1-dioxide 126-33-0 10.00%

Chemical Book, Sulfolane Basic information, Sulfolane CAS = 126-33-0

Valero Wilmington Refinery RMP 2014: MHF 10% Sulfolane to reduce HF vapor Valero adopted the ReVAP brand of MHF (developed by Mobil/Phillips, now owned by Honeywell) in 2005

<u>WHY DEMAND MHF "TRADE SECRETS" IF WE ALREADY KNOW WHAT THEY ARE?</u> For "credibility" and to eliminate uncertainty. When official data is withheld, Jill Public is easily accused of not knowing what she's talking about.

-The MHF additive concentration in 1990 was 50%-

Former Torrance City Councilman Don Lee, 1992-2000, ExxonMobil Community Advisory Panel mtg. 11/17/2015, "[The concentration] started at 50% [in 1990] then settled at 30% [in 1994]."

		~~~~	
			140 psig
Addi	Temper-	Impact Plate	
itive	*!ure	& Pad	Rainout
wt %	* <b>F</b> .	Yes/No	W1 %
•		4. 44	4
50	***	***	99
	HF// Addi itive wt %	HF/Additive Ter Addi Temper- itive sture wt % *F.	Addi Temper- Impact Plate itive ature & Pad wt % *F. Yes/No

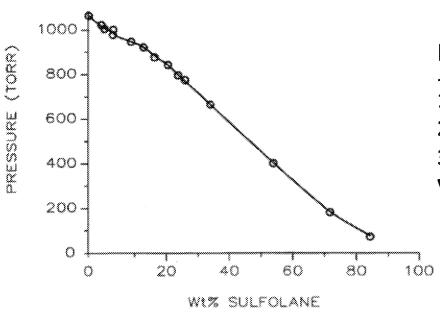
TECHNICAL DATA. 2/14/1994 Mobil Patent 50% additive achieves only 64% rainout (~ARF) Proprietary barriers (impact plate & pad) had to be installed to increase rainout to 99%

The 1990 Consent Decree Condition for MHF acceptance was that "no dense vapor cloud" of HF should form upon accidental release of MHF, that is,  $\sim$ 100% ARF. Clearly, this would have required the use of 50% additive plus proprietary barrier technology. That is, if MHF with 50% additive had been a viable option, which it was not.

US Patent, 1992, Mobil Oil Corporation, Containment of an Aerosolable liquid jet, US5286456, filing date 24 Sep 1992. <a href="http://www.google.com.sv/patents/US5286456">http://www.google.com.sv/patents/US5286456</a>.

-The MHF additive concentration in 1995 was ~30%-

Former Torrance City Councilman 1992-2000, ExxonMobil Community Advisory Panel, 11/17/2015, "[The concentration] started at 50% then settled at 30% [by 1995]."



#### **EVIDENCE FROM TECHNICAL DATA**

- 1. 1995 SA REPORT 65% ARF
- 2. 2015 Workshop: 88°F MHF boiling pt.
- 3. 1995 Phillips US MHF Patent, Vapor pressure curve HF-sulfolane.

Curve is an isotherm at 86°F. The boiling point of MHF is 88° F (Torrance Workshop SA report), which is close to 86° F. At 760 torr (atmospheric pressure) the Sulfolane percentage is around 30%.

ReVAP European Patent EP 0796657 B1, "Alkylation catalyst containing hydrofluoric acid and a sulfone," Phillips Petroleum Company, 1992, <a href="http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en\_EP>.">http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en\_EP>.

Sally Hayati, TRAA

-The MHF additive concentration in 1995 was ~30%-

	HF//	Ndditive Te	ts Pressure:	ressure: 140 psig		
HF concentration wt %	Addi itive wt %	Temper- ature *F.	Impact Plate & Pad Yes/No	Rainout wt %		
50 <b>5</b> 0	50 50	110 110	N Y	64 99		
66	34	90	N	53		

1994 Stipulation and Order: MHF should achieve 65% ARF using 30% additive.

Industry data indicates that 34% additive at low temperature achieves only 53% rainout (~ARF) without proprietary barriers (impact plate & pad). 30% would get less. Higher temperatures result in greater airborne acid & possibly aerosol formation.

YET, the 1995 SA report does not describe the installation of impact plates & pads. The first indication of proprietary barrier technology being installed is in 1998.

US Patent, 1992, Mobil Oil Corporation, Containment of an Aerosolable liquid jet, US5286456, filing date 24 Sep 1992. <a href="http://www.qoogle.com.sv/patents/US5286456">http://www.qoogle.com.sv/patents/US5286456</a>.

-Additive concentration was reduced by a factor of 3 in 1998, to 10%-

SOURCE 1: Torrance Refinery Safety Advisor Project, Steve Maher, "Evaluation of MHF Alkylation Catalyst (Analysis of proposed additive concentration changes)," 10/1999

This report reveals that the additive concentration was reduced in 1998

SOURCE 2: Honeywell MHF Material Safety Data Sheet (MSDS). The monopoly manufacturer of MHF. <a href="http://bit.ly/21T6yAt">http://bit.ly/21T6yAt</a>

- Hydrofluoric acid 90.00% (also 85%)
- Sulfolane (THT) 10.00% (also 15%)

#### SOURCE 3: Honeywell via PBF

- Since a range of 10-15% is given, it is highly likely the concentration used is 10%, Otherwise, Honeywell would say just 15%
- Note: XOM claims a higher additive %
  is maintained during transport. They may
  purchase 15% but use 10% or less during
  processing

# WHAT IS MODIFIED HYDROFLUORIG (MHF) ACID? Modified Hydrofluoric Acid (MHF) is HF that contains an additive that lowers the volatility of the original compound ✓ Reduces risk of exposure in the event of an MHF leak or spill The MHF used at the Torrance refinery is designed to reduce the volatility, or vapor potential, of hydrofluoric acid and features an additive that can reduce the volatility by 60 to 90 percent ✓ The MHF delivered to the refinery contains the industry standard of approximately 10 to 15 percent concentration of this additive

SOURCE 4: Valero Wilmington Refinery Risk Management Program Report 2014 (adopted same MHF in 2005)

Worst-Case Toxic Sce	narios 🖲
Physical State	Gas liquified by pressure
Model Used	SLAB Model
Sumps	
Passive Mitigation - Other	10% sulfolane additive to reduce the HF to form an aerosol on release under pressure to atmosphere. "Diffuser" or Barrier ground flange.
Confidential Business Information	No

- MHF with ≤ 20% additive is described as "fuming," like HF-

In ReVAP MHF's European patent submitted by Phillips (Mobil's co-developer) test data is given for additive concentrations from 20% to 50%. No data is given for additive at any lower concentration, since that was too low to confer any "safety" advantage over HF.

ReVAP European Patent EP 0796657 B1, "Alkylation catalyst containing hydrofluoric acid and a sulfone," Phillips Petroleum Company, 1992, <a href="http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en EP>.">http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en EP>.

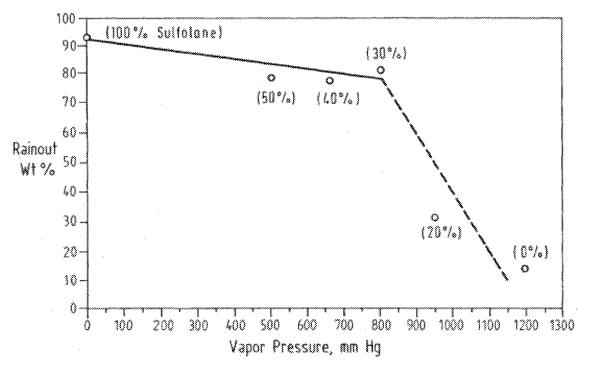
Example	1	2	3	4
Catalyst		HF/ Sulfolane (80/20)	HF/ Sulfolane (60/40)	HF/ Sulfolane (50/50)
Appearance	(Fuming)	Fuming	Liquid	Liquid

Example column 2 is MHF with 20% additive (Sulfolane) and 80% HF

- Its appearance is "fuming," just like HF's. NOT SAFE.
- ≥ 40% additive, however, appears as a liquid. SAFER.

Phillips notes, "Alkylate quality... decreased with further Sulfolane" above 20% and catalyst activity ceases if additive concentration is higher than 50%. MHF isn't viable.

-Airborne acid reduction (ARF) is now < 20%. >80% released acid becomes airborne-



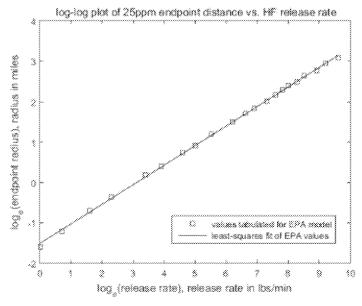
#### **EVIDENCE**

- Additive is now at 10%
- 2. Phillips 1995 US MHF Patent,
  - a. Vapor pressure curve
  - b. Rain-out curve HFsulfolane

The rainout for anhydrous HF is inexplicably high on this graph (15%). Should be close to 0%.

ReVAP European Patent EP 0796657 B1, "Alkylation catalyst containing hydrofluoric acid and a sulfone," Phillips Petroleum Company, 1992, <a href="http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en\_EP>.">http://worldwide.espacenet.com/publicationDetails/originalDocument?CC=EP&NR=0796657B1&KC=B1&date=&FT=D&locale=en\_EP>.

-ARF achieved by MHF with 10% additive is 15%-

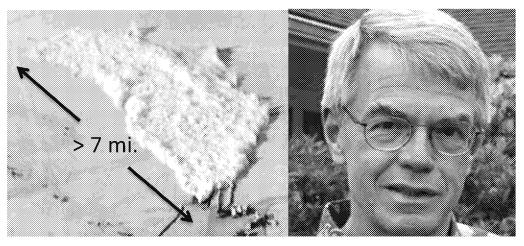


Evidence: ARF for 10% MHF = 15%

- 2004 EIR for Valero Refinery MHF unit
  - MHF "results in a 7.9% reduction in the... downwind travel of HF... clouds."
  - Same MHF used by ExxonMobil (ReVAP)
- Observation & analysis by Dr. Toni Churg
   Graph of EPA Table 7 (L) shows linear log<sub>e</sub>-log<sub>e</sub> relation between toxic radius & release rate
- $log d = c + s \times log M$  because  $log_e log_e$  plot is linear. So:  $d = e^c \times M^s$   $d = endpoint radius (Y-axis); M = release rate (X-axis); c = Y-axis intercept; s = Slope = <math>\frac{1}{2}$
- $d_2/d_1 = (e^c \times M_2^s)/(e^c \times M_1^s) = M_2^s / M_1^s = (M_2 / M_1)^s$
- $(d_2/d_1)^{(1/s)} = (0.921)^2 = 0.8482 = (M_2/M_1)$ 
  - $M_1$  = release rate of MHF,  $M_2$  = "effective HF release rate" for MHF (lower than  $M_1$  by ARF %)
  - $d_1$  is the distance for an equivalent HF release,  $d_2$  is MHF distance, which is **7.9% shorter than d\_1**.
  - 1.00 .079=0.921; so  $(d_2/d_1)$  =0.921; 1/s = 2; 1.00 0.8482 = 0.1518. M<sub>2</sub>=15% smaller than M<sub>1</sub>

#### Top HF Expert Says it's Worse than That

-The Airborne Reduction Factor achieved by MHF with 10-20% additive is only 10%-



#### Ronald P. Koopman Ph.D., P.E.

- Former Liquid Gaseous Fuels
   Program Leader at the Lawrence
   Livermore Laboratory
- Hydrofluoric acid expert
- Test Director on 1986 Goldfish HF Release Tests & 1988 Hawk Tests

#### Personal email, sent Dec 17, 2015 at 1:03 PM

- If 10% or 20% [additive] Sulfolane is used there is very little difference between HF and MHF... in terms of concentration and travel distance downwind.
- At 10% concentration there is only 10% rainout... 90% of the MHF travels downwind.
- [10% additive poses] a much bigger hazard [than 30% additive].

#### Just a Few Weaknesses of Mobil's Barrier Theory

- MHF performance claims for different additive levels assumed use of the same technology
  - The refinery is improperly taking double credit for the questionable benefits of this barrier technology.
  - MHF test setup included a "proprietary barrier technology" to enhance acid fallout (SA 1995 Consent Decree rpt)
  - MHF ARF claims are valid only with these barriers ("impact plate & pad" in 1992 MHF barrier patent table below).
  - The 1997 MHF unit design didn't include barriers and could not have achieved Mobil's promised 65% reduction.

***************************************	HF/Additive Tests Pressure: 140 psig			US Patent, 1992, Mobil, Containment Aerosolable liquid jet,		
Test No	HF concentration wt %	Addi itive wt %	Temper- ature *F.	Impact Plate & Pad Yes/No	Rainout wt %	<http: patents="" us5286456="" www.google.com.sv="">.</http:>
34	50	(50)	110	N	64	1990 claim: 50% add $ ightarrow$ 100% rainout
36	50	50	110	Y	99	
33	66	(34)	90	N	53	1994 claim: 30% add → 65% rainout
37	69	31	90	Y	94	

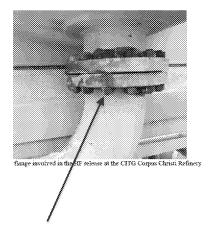
- Collection pans w/water were used to achieve the performance claimed during MHF tests
  - The claim was that water stopped vaporization. Yet the new 1998 MHF unit design does not include pans with water.
  - After falling to the ground, rained out acid will rapidly form a vapor w/ some droplets
  - Rained out acid still becomes airborne although at a slower rate. Some cloud concentration reduction is only benefit.
  - Even water in the collection pan can't stop vaporization. Only a chemical reaction could do so. (per Dr. Ron Kooman)
- Many/most release locations on the MHF unit have no barriers
  - Only the Acid Settler Tank bottoms and acid circulation pumps have barriers
  - The top of the settler tanks and associated piping plus all other pipes, flanges and the reactor, etc., have no barriers
- Barriers could be damaged by the same mechanisms that cause an MHF release
- There's been no independent verification of Mobil's barrier theory claims.
  - Tests never performed on MHF w/ 10% additive & barriers 1-3" from the release point.

Sally Hayati, TRAA

### **Barrier Types & Locations**

- Acid settler bottoms
  - Metal shields at bottoms of acid settler tanks w/ high levels MHF (p. 5)
  - Distance: 3 inches (p. 85)
- Seals of acid circulation pumps
  - Complete metal barriers (p. 5) at a distance < 1 inch (p. 85)</li>
- Flange shrouds for pipes: So dodgy, Mobil abandoned this barrier type at the last moment.
  - Clear polymer shields (p. 5) PVC (p. 29) like Vue-Drain-Gard safety Shields, w/ stainless steel clamps
  - Teflon side shielding materials; Distance: < 1 inch (p. 85)</li>
  - Stainless steel demister pads are wired into the Safety Shield's drain port (p. 33)
    - Designed to remove micron-size liquid particles from a stream consisting of liquid and vapor
    - As velocity and liquid loading increases, a demister pad will become flooded.
  - Initially, Mobil claimed a risk credit of 27% from use of these flimsy clear plastic shields
  - But at the last minute, "Rigorous pursuit of flange shrouding credits could not be justified" (P. 43)
  - JUST A FEW OF THE PROBLEMS
    - Ramco, manufacturer: "RAMCO Safety Shields are suitable exclusively for liquid chemicals... [They] have not been designed for use with gases ...and... should not be considered for [this] application. ...[their] purpose is to ... deflect temporarily the escaping fluid."
    - SA: "Initial field tests indicated that, during a release, some materials might exit through the seams." (p. 29)
    - SA: there are "inherent uncertainties in this new application for flange shrouds, and ... discrepancies between technical literature and this particular application." (p. 20), including "incompatibility of flange shroud materials with HF. ...[Yet] Use of these materials ...is... acceptable [to the SA], with the provision of ...diligent operations personnel field surveillance of flange shroud integrity and periodic materials testing." (p. 29)

Page references all from Safety Advisor's (SA) 1999 report, <a href="http://bit.ly/1Nzic8W">http://bit.ly/1Nzic8W</a>.



# Deception, Lack of Testing and Documentation, Lack of Scientific Rigor for Mobil's 1998 Claims

- Mobil attempted to claim lower airborne HF rates for all releases everywhere, even at non-barriered locations
  - Mobil's "initial calculations ...credited reductions in airborne release fractions for all releases" [not just those at locations w/ barriers]
  - Mobil credited all settler releases and all settler spool releases with lower acid airborne rates, even those not mitigated by Acid Settler Pans (interim measure)
- Testing was never performed on MHF with additive concentrations below 21% or at barrier distances less than 8 in.
- Mobil-developed SW model used to determine barrier performance
  - not accurate for the very close barrier spacing used
  - not accurate for MHF w/ 10% additive because of flash atomization (formation of aerosol)
  - assumed the presence of water in collection trays (not used at Torrance)
- Many decisions & evaluations were not backed by data analysis
  - "the shroud is fairly 'tough,'" "the SA feels that..." the use of fudge factors to correct model inaccuracies produced a "reasonable" result

## Quantitative Risk Analysis: a Poor Tool

- Pretense of more quantitative knowledge than available
  - approximately 20% of critical pump leaks involve seals/ gaskets; but the severity or leak size is unknown. (p.40)
  - Determining potential leakage rates outside of the proposed shrouded/barriered area is inaccurate. (p.40)
- Negligible risk contributors (p.39 SA '99 rpt): low probability assigned, so the risk can be ignored
  - Risk weighting is standard practice for consequences that are too great to tolerate, but SA said that was outside of scope
- Mobil's hand-picked Consent Decree Safety Advisor (SA):
   TRUST, DON'T VERIFY. SA Mobil